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(54) Synthesising a polysilane

(57) A polysilane of formula
 $-(\text{SiH}_n-)_x$ where n is 1 or 2 and
 x is large (10, 20 or more) may be
a precursor of amorphous silicon
films and is synthesised by treating
 $\text{SiH}_m\text{X}_{4-m}$, where m is 1, 2 or 3
and X is halogen, preferably
 SiH_2Cl_2 or SiHC1_3 , with lithium
suspended in a liquid inert to the
reagents and non-solvent for the
polysilane, preferably tetrahydrofu-
ran.

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SPECIFICATION

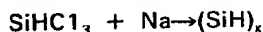
Synthesising a polysilane

5 This invention relates to a method of synthesising an unsubstituted polysilane, having an approximate composition of $-(\text{SiH}_n-)_x$ where x is large (such as at least 10) and n is from 1 to 2.

10 Unsubstituted polysilanes are potential precursors for hydrogenated amorphous silicon films. These films have properties such as photoconductivity and could be used in zero-graphy, image intensifiers and photovoltaic devices including solar cells, which may com-
15 prise films of such amorphous silicon on substrates. Such solar cells promise to offer the important advantage of moderate cost for large areas at reasonable efficiencies.

20 Various syntheses for polysilanes are already known. Some have as their starting material such compounds as $(\text{SiBr}_2)_x$ or Si_5H_{10} , which are not commercially available, thus adding to the number of steps necessary.

25 Another has as its starting material SiHBr_3 , which as generally prepared is said to be explosive. A typical known synthesis, reported by Stock and Zaidler in *Berichte*,
30 56B(1923)986, is



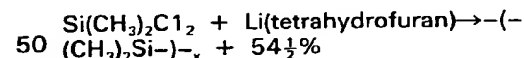
but as the sodium is in the form of amalgam, separation of the product is difficult.

35 Another typical known synthesis, reported by Stock and Somieski in *Berichte*, 56(1923)247, is



40 but the yield is small (theoretical maximum $2/3x$), the principal product being monosilane, which can explode on contact with air.

45 Another synthesis, but intending to lead to a variety of substituted ring compounds, is reported by Matsumura, Brough and West in *JCS Chemical Communications* 1978 p1092:



ring compounds.

55 According to our invention, a method of synthesising an unsubstituted polysilane (of approximate composition $-(\text{SiH}_n-)_x$ where x is large and n is from 1 to 2) comprises reacting $\text{SiH}_m\text{X}_{4-m}$, where X is fluorine, chlorine, bromine or iodine and $m = 1, 2$ or 3,
60 with lithium in a suspension of liquid inert to the reagents and the product and in which the polysilane is insoluble.

X is preferably chlorine. x is preferably at least 10. m is preferably 1 or 2, particularly 2.

65 The molar ratio of lithium: $\text{SiH}_m\text{X}_{4-m}$ should

exceed $(4 - m): 1$ and is preferably at least $2\frac{1}{2}(4 - m): 1$ (i.e. 5:1 for dihalosilane). The weight ratio of the lithium to the liquid may be for example 1:90.

70 The liquid is preferably one in which the LiX also produced is soluble, and is preferably present in an amount sufficient to dissolve all the LiX that will be produced. A suitable liquid is tetrahydrofuran.

75 The invention will now be described by way of example.

EXAMPLE 1

Lithium (0.3g; 0.04 mol) was suspended in
80 30 cm³ (27g) rigorously dried and degassed tetrahydrofuran. This was reacted in the absence of moisture and air with gaseous dichlorosilane SiH_2Cl_2 (0.20g; 0.002 mol; initial partial pressure at room temperature 400
85 torr.)

An orange air-sensitive powder eventually precipitated (in our case after 18 hours) and was removed from the suspension in not more than 24 hours in order to minimise further
90 reaction of the powder. The powder fell to the bottom while the lithium tended to remain at the top; this aided separation. The tetrahydrofuran when subsequently exposed to air showed no reactivity, and this implies that

95 silane ring compounds (which would be soluble in tetrahydrofuran) were not formed to any significant extent. Also the lithium chloride which is produced in the reaction and which dissolves in the tetrahydrofuran could be precipitated from the latter by adding hexane to the tetrahydrofuran.

The orange powder was found by infrared spectroscopy to show spectral features closely analogous to thin films of hydrogenated amorphous silicon prepared by glow discharge
105 techniques. The powder is thus considered to be unsubstituted polysilane, of composition $-(\text{SiH}_n-)_x$ where n is approximately 2; x (from other evidence) appeared to be at least
110 20.

EXAMPLE 2.

Lithium (0.3g; 0.04 mol) was suspended in
115 30 cm³ (27g) rigorously dried and degassed tetrahydrofuran. This was reacted in the absence of moisture and air with liquid trichlorosilane SiHCl_3 (0.027g; 0.002 mol) at room temperature. The trichlorosilane appeared to be miscible with the tetrahydrofuran.

120 A brown air-sensitive solid powder eventually precipitated (in our case after 18 hours) and was removed from the suspension in not more than 24 hours in order to minimise further reaction of the powder. The powder
125 fell to the bottom while the lithium tended to remain at the top; this aided separation. The tetrahydrofuran when subsequently exposed to air showed no reactivity, and this implies that silane ring compounds (which would be
130 soluble in tetrahydrofuran) were not formed to

any significant extent.

From infrared spectroscopy, the brown powder is considered to be unsubstituted polysilane, of composition $-(\text{SiH}_n-)_x$, where n is approximately 1. From other evidence, x appeared to be 20 or more.

CLAIMS

1. A method of synthesising an unsubstituted polysilane, having an approximate composition of $-(\text{SiH}_n-)_x$ where x is large and n is from 1 to 2, comprising reacting $\text{SiH}_m\text{X}_{4-m}$, where X is fluorine, chlorine, bromine or iodine and $m = 1, 2$ or 3 , with lithium in a suspension of liquid inert to the reagents and the product and in which the polysilane is insoluble.
2. A method according to Claim 1, wherein x is at least 10.
3. A method according to Claim 1 or 2, wherein X is chlorine.
4. A method according to any preceding claim, wherein m is 1 or 2.
5. A method according to Claim 4, wherein m is 2.
6. A method according to any preceding claim, wherein the liquid is one in which the LiX also produced is soluble.
7. A method according to Claim 6, wherein the liquid is tetrahydrofuran.
8. A method according to claim 6 or 7, wherein the liquid is present in an amount sufficient to dissolve all the LiX that will be produced.
9. A method of synthesising a polysilane substantially as hereinbefore described with reference to Example 1 or Example 2.
10. A polysilane which has been synthesised by the method of any preceding claim.